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Katherine E. Robbins [1] *and Samuel Eddie Davis* [2]

Verification of the ASTM G-124 Purge Equation

ABSTRACT: ASTM G-124 seeks to evaluate combustion characteristics of metals in high-purity (>99%) oxygen atmospheres. ASTM G-124 provides the following equation to determine the minimum number of purges required to reach this level of purity in a test chamber: $n = -4/\log_{10}(P_a/P_h)$, where "n" is the total number of purge cycles required, P_h is the absolute pressure used for the purge on each cycle and P_a is the atmospheric pressure or the vent pressure. The origin of this equation is not known and has been the source of frequent questions as to its accuracy and reliability. This paper shows the derivation of the G-124 purge equation, and experimentally explores the equation to determine if it accurately predicts the number of cycles required.

KEYWORDS: purge equation, promoted combustion chamber, purge cycles, oxygen concentration, oxygen percentage, Dalton, partial pressures, high purity oxygen atmosphere

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[1] Student Researcher, Department of Mathematics, Vanderbilt University, 2201 West End Avenue, Nashville, TN 37240 USA

[2] Materials Engineer, Materials Combustion Research Facility, Materials Test Branch, NASA George C. Marshall Space Flight Center, Huntsville, AL 35812 USA

Introduction

ASTM G-124, *"Standard Test Method for Determining the Combustion Behavior of Metallic Materials in Oxygen-Enriched Atmospheres,"* was first approved in 1994 and is used internationally for comparisons of the combustion characteristics of various metallic materials. The combustion characteristics that can be evaluated include; lowest burn pressure, highest no-burn pressure, and regression rate (apparent burn rate) of the sample, among others. The intent of ASTM G-124 is to evaluate these characteristics of metals in high-purity (>99%) oxygen atmospheres. However, when conducting this test in a laboratory, the only guidance to reach this level of purity in a test chamber, where no greater than 0.01% of the original atmosphere is allowed to remain, is given by the following equation: $n = -4/\log_{10}(P_a/P_h)$, where "n" is the total number of purge cycles required (rounded up if not an integer), P_h is the absolute pressure used for the purge on each cycle, and P_a is the atmospheric pressure or the vent pressure. It is clearly useful to have such an equation because time and resources can be saved by knowing the correct number of purges required to reach the desired concentration of oxygen in a test chamber. However, the validity of this equation has, in the past, been called into question. Applications do exist where a difference of only a few tenths of a percent in the oxygen concentration can yield different combustion behaviors. Therefore, it is important that the origin and limitations of this equation are understood so that the equation can serve as a useful tool when performing testing per ASTM G-124.

Assumptions made:

This derivation and research utilize the simplifying assumption that the gasses involved behave ideally and compress as ideal gasses compress. This assumption is acceptable because the two gasses that dominate the performance of ASTM G-124, namely oxygen and nitrogen, do not behave in a manner that deviates significantly from the manner in which ideal gasses behave under the given conditions.

Experimental

Test Apparatus

All testing was conducted in promoted combustion chambers that are used by NASA – Marshall Space Flight Center to perform ASTM G-124 testing. Two chambers of different sizes and volumes were used to determine if chamber volume had any effect on the purges. Chamber 1 is a 10-liter (0.353 ft^3) promoted combustion chamber, and Chamber 2 is a 17-liter (0.60 ft^3) promoted combustion chamber.

Procedure

The procedures performed were identical when either Chamber 1 or Chamber 2 was utilized. Each chamber began the process by being sealed while in normal atmospheric air at ambient temperature and pressure, P_a. First, an initial oxygen concentration reading was taken from the air inside the chamber. Oxygen, as the purge gas, was then allowed to enter the chamber through a series of opening and closings of a valve until the chamber pressure was approximately the same as the desired purge pressure, P_h. The chamber was stagnant for a sufficient length of time to allow the temperature to return to near ambient, pressure to stabilize, and for the gasses to become a homogeneous mixture. This process typically took about three minutes. The stabilized pressure was recorded, and the chamber was then vented down to approximately 22.5 psia, or roughly 8 psia above atmospheric pressure. Samples of the gas inside the chamber were periodically removed from the chamber and analyzed by the oxygen analyzer until the oxygen concentration stabilized. This process was performed in order to determine the oxygen concentration of the gas in the chamber. The chamber was then vented down again to P_a, completing the first purge. The same process was repeated until the oxygen concentration either reached 100% or reached the maximum value that the oxygen analyzer could detect (i.e., when further purges did not increase the oxygen concentration reading on the instrument). After each series of analyses was complete, the chamber was emptied of gas, filled with atmospheric air, and a new purge cycle analysis was begun with the next P_h.

Derivation

The following symbolism is used throughout this derivation:

P_i – The partial pressure of the chamber gas mixture resulting from gas "i".

P_a – The partial pressure of the chamber gas mixture due to the initial chamber gas, normally air. This is also the lowest pressure that will be witnessed by the test chamber environment during the pressurization and venting cycles. This is typically atmospheric pressure, or the lowest chamber pressure witnessed.

P_h – The highest pressure that will be witnessed by the test chamber environment during the pressurization and venting cycles. It is the pressure resulting from the mixture of all of the gases inside the chamber.

X_i – The molar ratio of the initial gas *"a"* of the chamber gas mixture after the "i^{th}" purge.

n_i – The number of moles of the original chamber gas remaining after the "i^{th}" purge.

This derivation begins by assuming that, even though the assumption does not simplify the derivation, the chamber initially is filled with ambient air at atmospheric pressure and is purged using only oxygen gas (thus the symbolism related to air and oxygen).

This derivation uses two elementary laws of chemistry and physics:

Dalton's Law of partial pressures: $P_h = P_a + P_{O2}$

and

Ideal gas law: PV = nRT

Where P = Pressure, V = Volume, n = Number Moles of Gas, R = Gas Constant and T = Temperature

(Note: The Ideal Gas Law is assumed to be applicable, as noted earlier, because ASTM G-124 is almost always conducted using oxygen and nitrogen, which behave very similarly to ideal gases.)

The impetus that leads to this equation in ASTM G-124 is a direct result of the following sentence taken from the test method: "Pressurize and vent the chamber a sufficient number of times to ensure that no more than 0.01 % of the original atmosphere in the vessel remains." This proportion refers to the mole ratio of the original chamber gas versus the final chamber gases, i.e., the ratio of n_a versus n_h, or $\frac{n_a}{n_h}$.

Given that PV=nRT, or equivalently, n=PV/RT, the ratio becomes:

Proportion of air remaining: $$\frac{n_a}{n_h} = \frac{\left(\frac{P_a V_a}{RT_a}\right)}{\left(\frac{P_h V_h}{RT_h}\right)} = \frac{P_a V_a R T_h}{P_h V_h R T_a}$$

Since Volume and Temperature will not change, and since R is the Gas Constant, then the equation simplifies to:

$$\frac{n_a}{n_h} = \frac{P_a}{P_h} = X_1$$

This is convenient since the values of *Pa* and *Ph* can be measured with gauges on the test chamber. Therefore, the mole ratio value can be easily obtained.

Initial conditions

Start with n_0 moles of air at atmospheric (or ambient chamber) pressure, P_a.

Purges will be at a final, or highest, pressure of P_h using O_2 gas.

First purge

Pressurize – then vent to P_a

Dalton's Law of partial pressures: $P_h = P_a + P_{O2}$

Ideal gas law: PV = nRT

Molarity of air after first purge $= X_1 = (P_a / P_h)$

Since the chamber is vented to the original pressure, P_a, and both the temperature and volume of the chamber have remained constant, the total moles of the mixture of gases in the chamber are equal to n_0.

Therefore, the moles of air remaining $= n_1 = n_{total} X_1 = n_0 X_1$

Second purge

Pressurize – then vent to P_a

The total pressure in the chamber is equal to the partial pressures of the remaining air and the oxygen added during the current purge.

The molarity of air after second purge $= X_2 = \dfrac{(X_1 P_a)}{P_h} = (P_a / P_h)^2$

Again, the total number of moles of gas in the chamber is equal to n_0.

Moles of air remaining $= n_2 = n_{total} X_2 = n_0 X_2$

Proportion of air remaining $= \dfrac{n_2}{n_0} = X_2 = (P_a / P_h)^2$

Nth purge

$$\text{Proportion of air remaining} = \frac{n_N}{n_0} = X_N = (P_a/P_h)^N \tag{1}$$

Solving for N:

$$X_N = (P_a/P_h)^N$$

$$\log(X_N) = \log\left((P_a/P_h)^N\right) = N \cdot \log(P_a/P_h)$$

$$N = \frac{\log(X_N)}{\log(P_a/P_h)} \tag{2}$$

When $X_N = 0.01\% = 0.0001$, and log base 10 is used,

$$N = \frac{\log_{10}(10^{-4})}{\log_{10}(P_a/P_h)} = \frac{-4}{\log_{10}(P_a/P_h)} \tag{3}$$

Equation (1) and Equation (2) are themselves valuable since they are more general forms of the Purge Equation and allow for a variety of conditions.

Data and Analysis

Step by step calculations

In order to look more closely at the data, it is useful to consider each purge individually, especially because of the difficulty in purging at exactly the same P_h each time. Equation (3) above was modified slightly for the actual experiment. This modification was performed to correct for the inherent errors that would creep into the equation because the initial chamber atmosphere is air, with 20.9% oxygen, and the purge gas was oxygen. The equation, taking into consideration oxygen in both the initial chamber air and purge gas becomes:

$$G = X_N \cdot G_0 + (1 - X_N) \cdot C \qquad (4)$$

Where, G is the final oxygen concentration,

G_o is initial oxygen concentration,

X_N is the proportion of original atmosphere left in the chamber after N purges, and

C is the oxygen concentration of the purge gas.

From Eq.1, for a single purge $X_1 = (P_a / P_h)$, so after a single purge:

$$G = (P_a / P_h) \cdot G_0 + (1 - (P_a / P_h)) \cdot C \qquad (5)$$

Equation (5) was used to generate the O_2% predicted by the purge equation after each single purge. Using this method, a situation where errors would quickly become compounded because of variations in P_h from purge to purge was avoided.

TABLE 1 - Purge data from Chamber 1 and 2

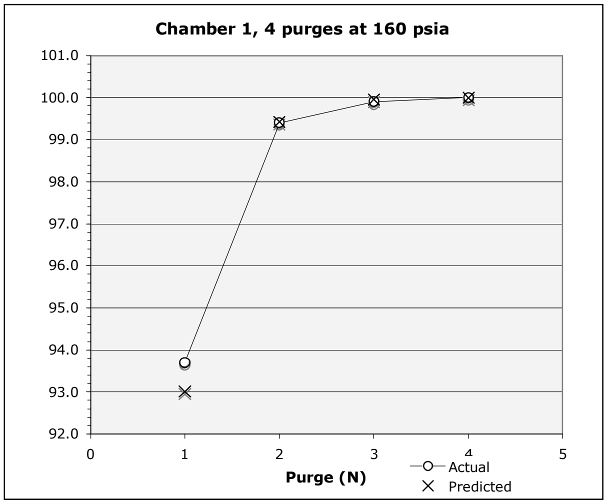
Chamber 1					Chamber 2				
Purge #	P_a	P_h	O_2%	Predicted O_2%	Purge #	P_a	P_h	O_2%	Predicted O_2%
0			20.5	20.5	0			20.8	20.8
1	14.7	82.7	88.7	85.86	1	14.82	89.82	86.8	86.85
2	14.7	94.7	98.1	98.24	2	14.82	89.82	97.7	97.74
3	14.7	85.7	99.5	99.67	3	14.82	95.82	99.5	99.56
4	14.7	88.7	99.7	99.92	4	14.82	91.82	99.8	99.84
5	14.7	128.7	99.8	99.97	5	14.82	98.82	99.9	99.89
0			20.5	20.5	0			20.8	20.8
1	14.76	167.76	93.7	93.01	1	14.82	163.82	93.0	92.74
2	14.76	159.76	99.4	99.42	2	14.82	173.82	99.1	99.31
3	14.76	164.76	99.9	99.95	3	14.82	177.82	99.7	99.83
4	14.76	158.76	100.0	99.99	4	14.82	162.82	99.8	99.88
0			20.5	20.5	0			20.8	20.8
1	14.76	280.76	96.3	95.82	1	14.82	268.82	95.6	95.54
2	14.76	270.76	99.8	99.80	2	14.82	266.82	99.5	99.66
3	14.76	274.76	100.0	99.99	3	14.82	269.82	99.7	99.88
0			20.5	20.5	0			20.7	20.7
1	14.76	441.76	97.7	97.34	1	14.79	441.79	97.2	97.06
2	14.76	451.76	99.9	99.92	2	14.79	408.79	99.7	99.80
3	14.76	445.76	100.0	100.00	3	14.79	416.79	99.8	99.89
0			20.5	20.5	0			20.7	20.7

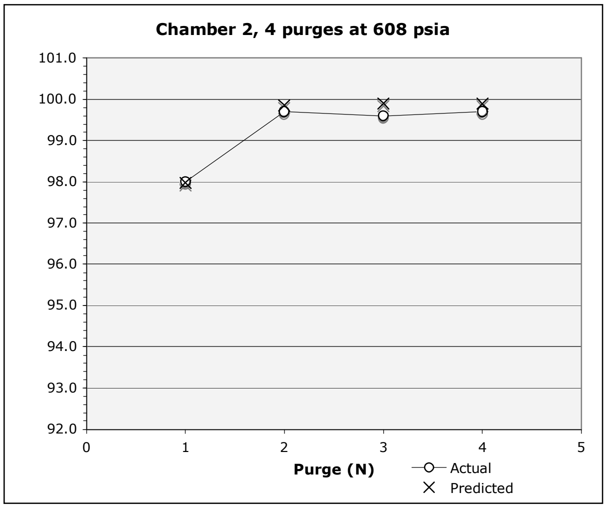
1	14.76	628.76	99.1	98.13	1	14.79	608.79	98.0	97.98
2	14.76	640.76	99.8	99.98	2	14.79	604.79	99.7	99.85
3	14.76	620.76	99.9	100.00	3	14.79	608.79	99.6	99.90
					4	14.79	608.79	99.7	99.89
	~~					~~~~~~~~~~~~~~~~~~~~~~~~~~~~~			
0			20.5	20.5	0			20.6	20.6
1	14.76	809.76	98.7	98.55	1	14.8	820.8	98.4	98.47
2	14.76	807.76	99.9	99.98	2	14.8	929.8	99.7	99.88
					3	14,8	809.8	99.8	99.90
	~~					~~~~~~~~~~~~~~~~~~~~~~~~~~~~~			
0			20.5	20.5	0			20.6	20.6
1	14.76	1025.76	98.9	98.86	1	14.8	1016.8	98.8	98.75
2	14.76	1014.76	99.8	99.98	2	14.8	1024.8	99.8	99.88
3	14.76	1015.76	99.9	100.00					
	~~					~~~~~~~~~~~~~~~~~~~~~~~~~~~~~			
0			20.5	20.5	0			20.5	20.5
1	14.76	1513.76	99.3	99.22	1	14.76	1513.76	99.3	99.22
2	14.76	1515.76	99.7	99.99	2	14.76	1515.76	99.7	99.99
3	14.76	1511.76	99.8	100.00	3	14.76	1511.76	99.8	100.00
	~~					~~~~~~~~~~~~~~~~~~~~~~~~~~~~~			
0			20.5	20.5	0			20.7	20.7
1	14.76	2027.76	99.5	99.42	1	14.8	2014.8	99.7	99.32
2	14.76	2026.76	99.9	100.00	2	14.8	2014.8	99.8	99.90
					3	14.8	2014.8	99.9	99.90
	~~					~~~~~~~~~~~~~~~~~~~~~~~~~~~~~			
0			20.5	20.5	0			20.6	20.6
1	14.8	5014.8	99.9	99.77	1	14.8	5014.8	99.5	99.67
					2	14.8	5014.8	99.7	99.90

	3	14.8	5014.8	99.8	99.90

Graphs

The graphs below show a plot of the actual O_2% and the predicted O_2% vs. the purge number. The actual versus predicted points align very closely together. The average difference between these points is reported as ‘avg. D’ in Table 2 for Chamber 1 and Table 3 for Chamber 2.





Results

Below is a summary of the data obtained for the two chambers. The average P_h over the series of purges is shown for convenience. However, the average P_h was not used for any calculations since the purges were analyzed individually, step by step. An asterisk is present if the actual number of purges required to reach the final O_2% was more than the number predicted by the purge equation. The column 'avg. D' lists the average difference between the actual and the predicted O_2% per purge.

TABLE 2 - Summary for Chamber 1

P_a, psia	avg. P_h, psia	Purges	Initial O_2%	Final O_2%	Purges predicted[2]	avg. D, %	D < 0.1% ?	D < 0.2% ?
14.7	96.1	5	20.5	99.8	4*	0.7080[3]	No	No
14.76	162.76	4	20.5	100.0	4	0.1900	No	Yes
14.76	275.43	3	20.5	100.0	4	0.1600	No	Yes
14.76	446.43	3	20.5	100.0	3	0.1300	No	Yes
14.76	630.09	3	20.5	99.9	2*	0.4167	No	No
14.76	808.76	2	20.5	99.9	2	0.1150	No	Yes
14.76	1018.76	3	20.5	99.9	2*	0.1067	No	Yes
14.76	1513.76	3	20.5	99.8	2*	0.1900	No	Yes
14.76	2027.26	2	20.5	99.9	2	0.0900	Yes	Yes
14.8	5014.80	1	20.5	99.9	2	0.1300	No	Yes

TABLE 3 - Summary for Chamber 2

P_a, psia	avg. P_h, psia	Purges	Initial O_2%	Final O_2%	Purges predicted	avg. D, %	D < 0.1% ?	D < 0.2% ?
14.82	93.22	5	20.8	99.9	4*	0.0400	Yes	Yes
14.82	169.57	4	20.8	99.8	3*	0.1700	No	Yes
14.82	268.49	3	20.8	99.7	2*	0.1333	No	Yes
14.79	412.46	3	20.7	99.8	2*	0.1100	No	Yes

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[2] Purges predictions were obtained by rearranging equation (4) to solve for $X_{N,}$ then substituting into equation (2).

[3] The high value for D at low pressures in Chamber 1 may be a result of poor mixing, since less turbulence has been observed in Chamber 1.

14.79	607.79	4	20.7	99.7	2*	0.1650	No	Yes
14.80	853.47	3	20.6	99.8	2*	0.1167	No	Yes
14.80	1020.80	2	20.6	99.8	2	0.0650	Yes	Yes
14.80	1514.80	3	20.5	99.6	2*	0.3733	No	No
14.80	2014.80	3	20.7	99.9	2*	0.1600	No	Yes
14.80	5014.80	3	20.6	99.8	2*	0.1567	No	Yes

The summary table above demonstrates that the purge equation typically did not predict the number of purges exactly. However, the prediction was almost always within one purge of the actual number of purges. One factor affecting the measured values is that the available oxygen analyzer did not have enough accuracy to allow $X_N = 0.01\%$. The oxygen analyzer only displayed one decimal place, so the smallest X_N that could be detected was 0.1% and this may have changed smaller inaccuracies into larger ones in later purges. Also, the average difference from the predicted oxygen percentage was not normally within 0.1%, but was typically within 0.2%.

Discussion of Uncertainties

Oxygen Analyzer and Purge Gas Purity

The largest contributors of uncertainty in this experiment were the inherent inaccuracies of the oxygen analyzer and the true oxygen concentration of the purge gas. The oxygen analyzer only displayed to one-tenth of one percent oxygen concentration. This created inaccuracies in that small changes of $O_2\%$ in the chamber could not be determined. These inaccuracies compounded as purges were repeated. Also, many of the purge cycles had readings that were above 99.0% and only one significant digit could change. The purity of the purge gas itself is also an issue because gas purity affects many calculations. The best available gas supply was only labeled by the vendor as "> 99.6%." For the calculations made here, an assumption was made that the purity of the purge gas was 100%. An assumption of 100% is required because running the purge gas though the oxygen analyzer typically produced readings of ~99.9/100%. However, it is possible that the purity was less at times. This would explain why purges in Chamber 1 could often reach 99.9% or 100%, while purges in Chamber 2 could only reach 99.8% or 99.9%.

Multiple Purges

Utilizing chambers that are designed to purge at high pressures often makes it difficult to stop the purge at an exact peak purge pressure, such as 80 psia. Because of this, each purge was analyzed individually rather than assuming a constant P_h over a series of purges. By using this method, deviations from the purge equation could be determined without the introduction of additional errors when the P_h values are not constant. This is a beneficial means of analysis, but, in actual applications, these small, individual errors would be compound though multiple purges. It should be noted that, in actual application, more purges lead to greater overall errors.

Pressure and Temperature

The test chamber temperature could not always be held at a constant level during the purge cycles, which led to other inherent compounded errors. Most notably, whenever purge gas was added to a chamber, both the pressure and the temperature would increase significantly.

Even though additional time was added to allow the temperature to drop back to normal prior to taking pressure readings, the temperature differential may have caused variations in the pressure readings, especially for higher pressures purges in which the temperature increases were more substantial.

Conclusions

The purge equation provides a good rough estimate for the number of purges required to reach a given gas concentration. In this study, the actual number of purges was within one purge of the number predicted by the purge equation in nineteen out of twenty independent tests. The equation itself holds up well with resulting deviations that are small, typically within 0.2% of the actual oxygen percentage for each purge. If accuracy to within a few tenths of one-percent is desired, then this test method requires using an accurate, calibrated oxygen analyzer to determine the oxygen concentration at each step. However, the test method given by ASTM G-124 rarely requires this level of accuracy. Therefore, the purge equation is a valuable tool that can be used to determine the number of purge cycles that are required to be performed prior to igniting a test sample in an ASTM G-124 test.